#### Phase Transformations - 3

### **Amorphization**

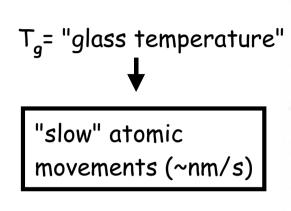
#### Harry Bernas

CSNSM, CNRS-UMR 8069, Université Paris XI 91405 - Orsay

bernas@csnsm.in2p3.fr

#### Outline:

- 1. Amorphous systems: thermodynamics, structural and *(some)* electronic properties
  - volume F.E. considerations
  - rôle of interfaces
  - rôle of strain
- 2. Phase transformations under irradiation *(open systems)*: non-equilibrium phase diagrams
- 3. Simple mechanisms for amorphization via irradiation
- 4. Ion beams: a microscope to study the amorphous state
  - reveals
- kinetics vs. thermodynamics
- amorphization mechanism is not unique
- rôle of (i) strain, (ii) interfacial energy



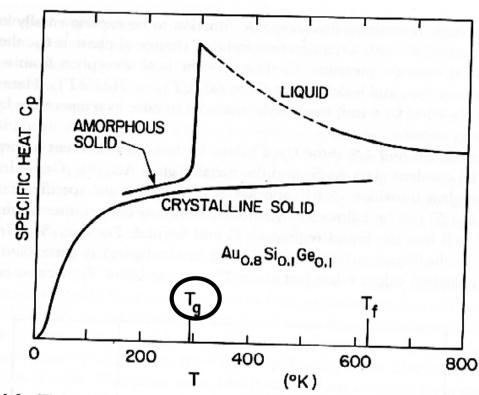
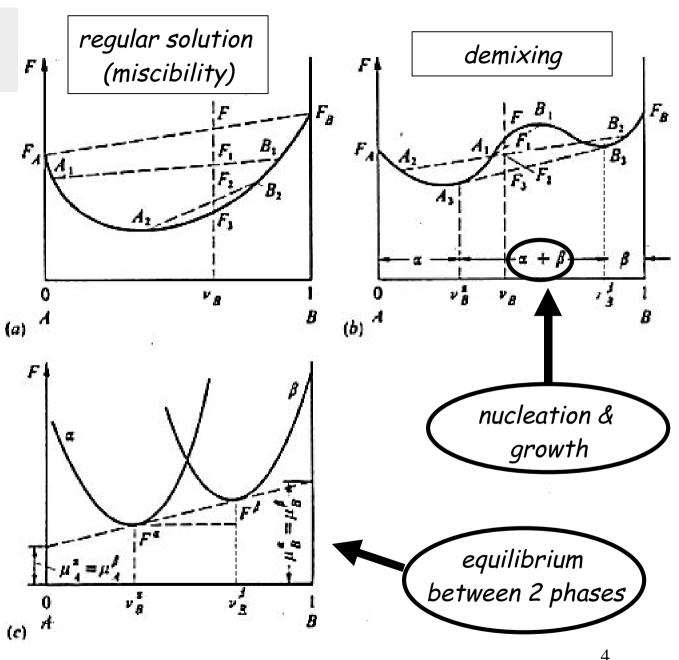


Figure 1.9 The specific-heat signature of the glass transition in a metallic glass (Chen and Turnbull, 1968).

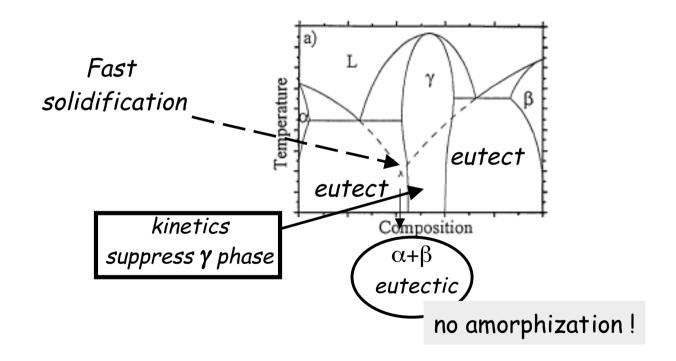
A phase transformation is NOT necessarily a phase transition. The glass transition is **not** a (thermodynamic) phase transition! It is a *kinetic* transition (configurational freezing)

(a reminder on ≠ F.E. cases)



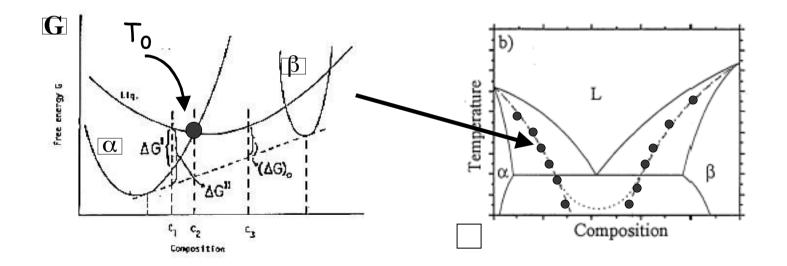
Radiation Effects in Solids, Erice July 18-28, 2004

#### an equilibrium phase diagram + fast quenching



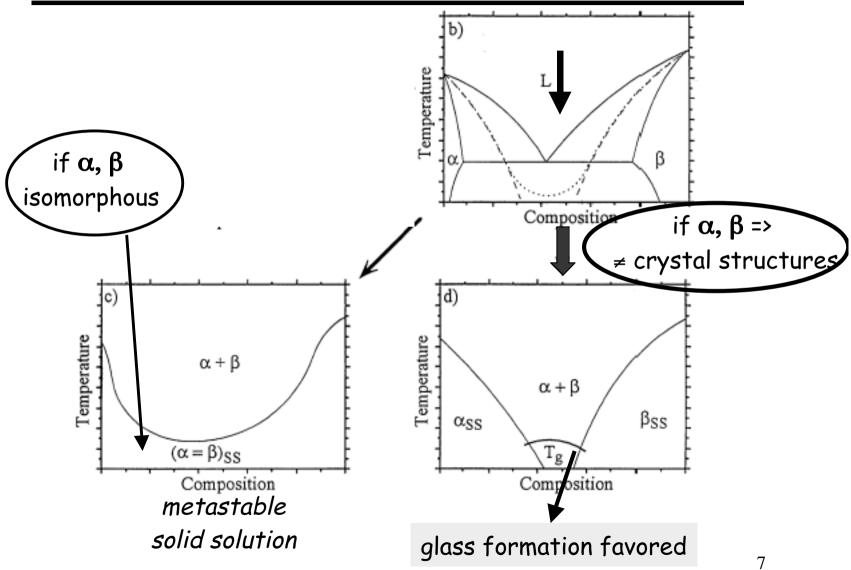
#### Glass Forming Ability (GFA) near deep eutectic

Define " $T_0$ " curve, such that  $\Delta G(\text{liq}) = \Delta G(\alpha \text{ phase})$ 



Typical free energy conditions in the region of autectic solidification at a temperature slightly higher than the glass transition temperature  $T_{\rm g}$ 

#### Glass Forming Ability (GFA) near deep eutectic



## Critical parameters for Glass Forming Ability (GFA)

- · Volume free energy
- Competition between ≠ structures

## Demixing condition (nucleation & growth)

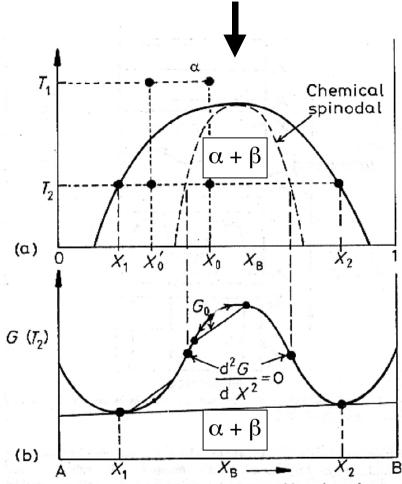
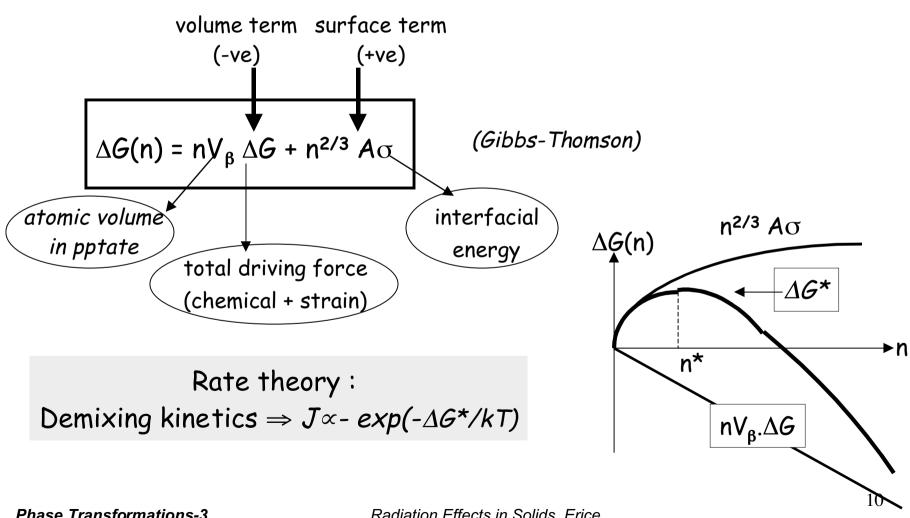


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phases  $\alpha_1$  and  $\alpha_2$  without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

#### Thermodynamics: phase separation

#### Classical nucleation theory:

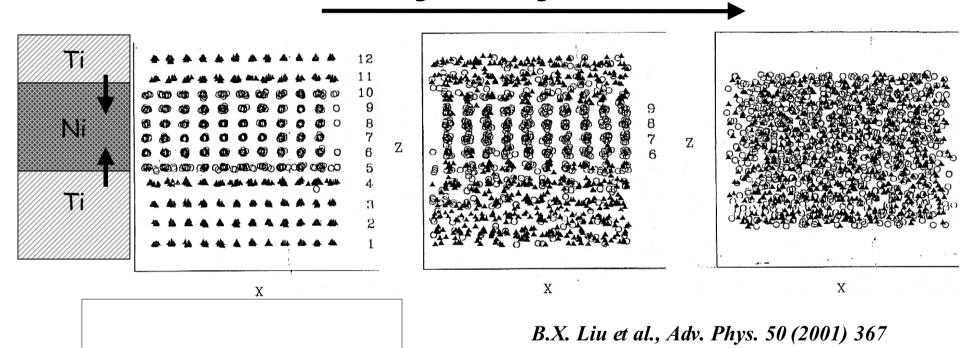
Formation of  $\beta$ -phase spherical cluster (n atoms) in  $\alpha$ -phase :



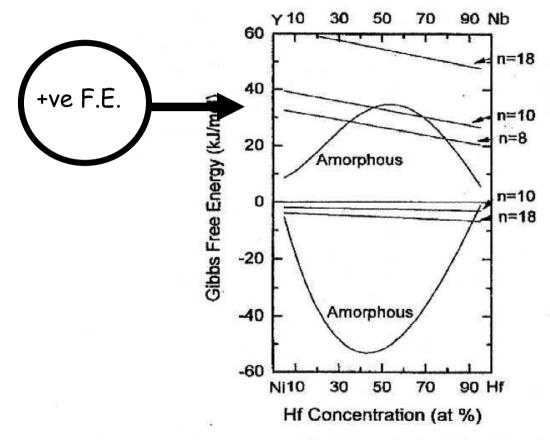
Phase Transformations-3 H. Bernas Radiation Effects in Solids, Erice July 18-28, 2004

#### Interfacial growth of amorphous phase = f(T)

## Molecular Dynamics simulation increasing annealing times @ constant T



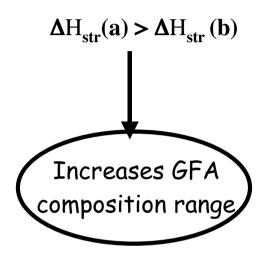
#### Rôle of interfacial energy



Calculated free energy diagram of the Nb-Y and Hi-Hf systems, showing different effects of interfacial free energy on alloy phase formation in the positive and negative heat of formation systems. n stands for the number of interfaces in the multilayers.

B.X. Liu et al., Adv. Phys. 50 (2001) 367

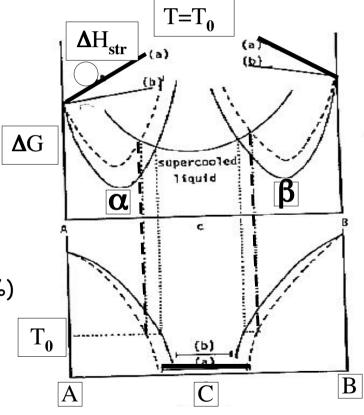
#### Enhancing GFA: effect of strain



Rôle of

component atomic size differences (>12%)

· interface mismatch (esp. @ nm scale!)

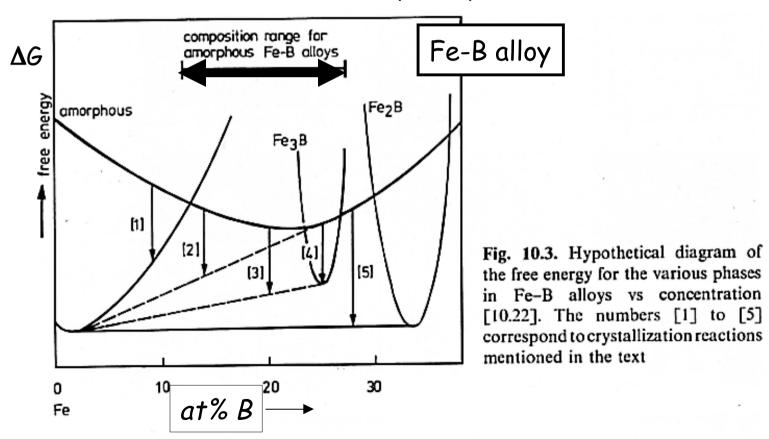


## Critical parameters for Glass Forming Ability (GFA)

- · Volume free energy
- Competition between ≠ structures
- Surface / interface energy
- Strain

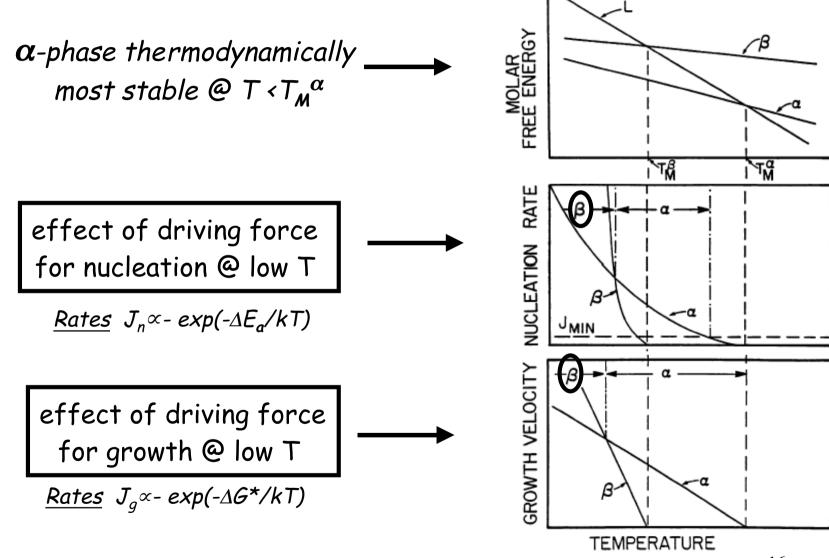
#### Enhancement of Glass Forming Ability (GFA) near deep eutectic

Presence of several phases with small  $\Delta G$  differences => competing structures (+ strain) favors amorphous phase formation



"Thermo*kinetics*" of amorphous systems

#### Enhancing GFA: competing phases



## Critical parameters for Glass Forming Ability (GFA)

- · Volume free energy
- Competition between ≠ structures
- Surface / interface energy
- Strain
- Relative nucleation and growth speeds

#### Pre-irradiation conclusions

- 1. Free energy vs. kinetics -
  - FE considerations => · GFA in deep eutectics
    - rôle of ≠ phase structures & strain
    - · nucleation & growth of a vs. c phase
    - GFA when competing phases => "frustration"

Note : on microscopic scale, atomic (+ vacancy) motion  $\Rightarrow V_p$ ,  $E_B$  ... (MD, KLMC...)

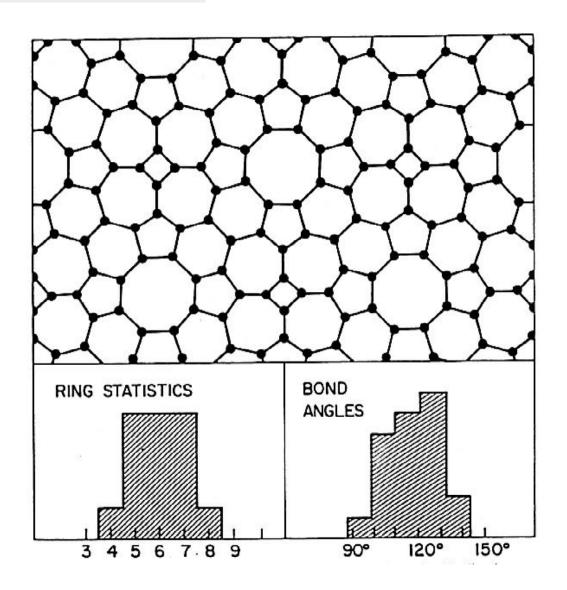
- 2. Rôle of chemical short range order (CSRO)
  - competing CSROs => favor GFA
  - CSRO in amorphous structures

- 3. Transport and magnetic properties
  - related to disorder and CSRO

#### Rôle of chemical short range order (CSRO)

"Amorphous" does **not** mean random!

- · well-defined CSRO
- Distribution of bond angles => (+/-) MRO



#### Amorphous structure: an experimental definition

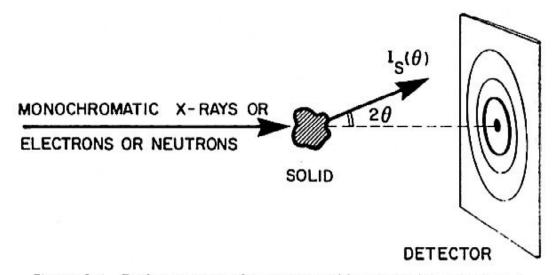


Figure 2.4 Basic geometry of structure-probing scattering experiments.

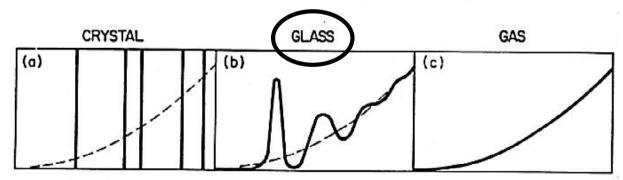
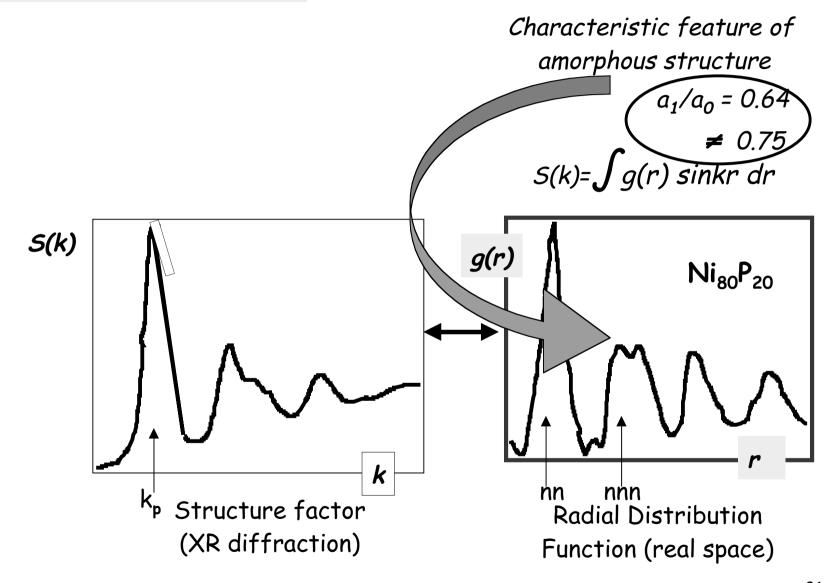


Figure 2.3 Schematic sketches of the radial distribution functions for (a) a crystalline solid, (b) an amorphous solid, and (c) a gas.

#### Amorphous structure



#### Amorphous structure

#### Probability of nn around A or B site

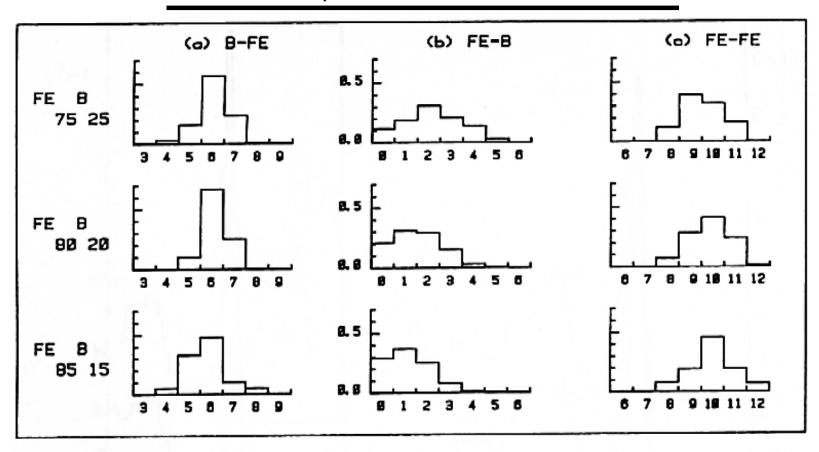
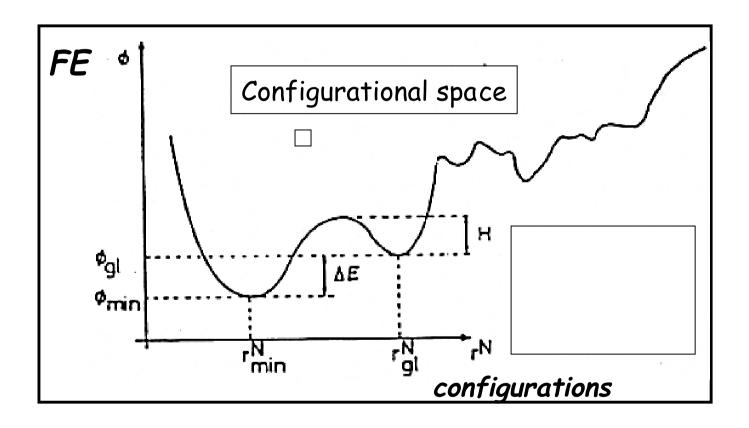


FIGURE 17. Probability distribution of the number of near-neighbors in models of Fe-B glass alloys. (a) Fe atoms around B atoms, (b) B atoms around Fe atoms, and (c) Fe atoms around Fe atoms. Near-neighbors are defined as atoms within the hard sphere touching distance  $\pm 10\%$ . (D. S. Boudreaux)

But as soon as one goes from CSRO to

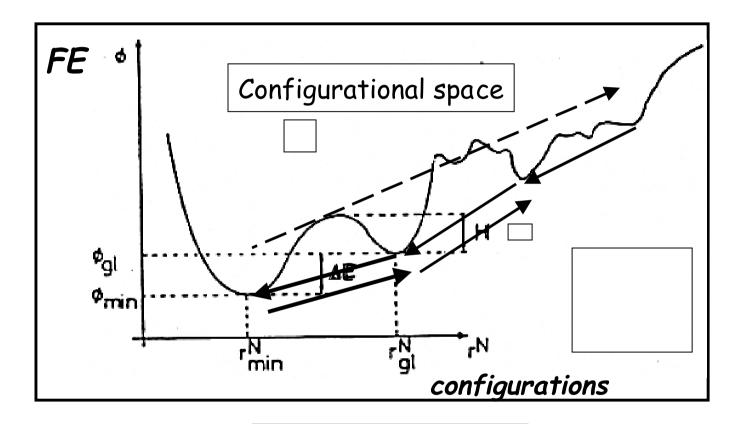
"Medium Range Order" (MRO)...

#### There are many different amorphous states ...



... and irradiation allows us to reach them

#### ... and annealing or irradiation allows us to travel among them



(No phase transition!)

#### Pre-irradiation conclusions

- 1. Free energy vs. kinetics -
  - FE considerations => · GFA in deep eutectics
    - rôle of ≠ phase structures & strain
    - nucleation & growth of a vs. c phase
    - GFA when competing phases => "frustration"

<u>To remember</u>: Consider  $\Delta G_0$  (stable phase) vs.  $\Delta G_1$  (metastable phase)

- If  $\Delta G_0 >> \Delta G_1$  => thermodynamics dominates
- If  $\Delta G_0 \sim \Delta G_1$  => kinetics determine phase formation
- 2. Twofold rôle of chemical short range order (CSRO)
  - competing CSROs => favor GFA
  - CSRO in amorphous structures
- 3. Transport and magnetic properties related to disorder and CSRO

Note: On a microscopic scale, all effects are related to atomic (+ vacancy) motion.

#### Effect of microstructure on transport properties

#### 1. Basics:

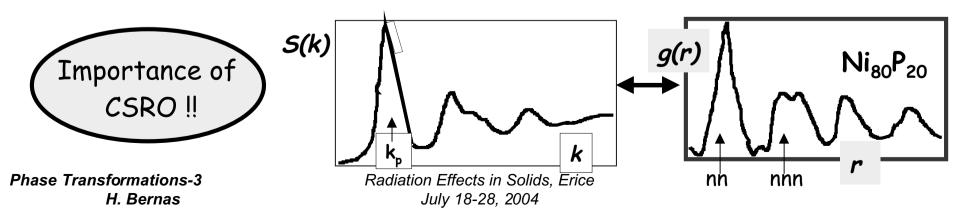
• Boltzmann equation:

$$\rho \sim [(e^2 v_F^2 N(E_F) \tau]^{-1}$$

• <u>for liquid metals</u>:  $(\rho \neq \text{random scattering}) e^-$  scattering by correlated ion distribution => coherence of diffracted waves. mfp is determined by Faber-Ziman (weak scatt'g, pseudopotential approx.)

$$\tau^{-1} = 1/h \int (1-\cos\theta) \left| \langle k \mid V \mid k' \rangle \right|^2 N(E_F)$$
 with  $V = \sum_i V(\underline{r} - \underline{R}_i) \implies \langle k \mid V \mid k' \rangle = [V(k)/N] \sum_i \exp(i\underline{k}.\underline{R}_i)$  Now 
$$(1/N) \left| \langle k \mid \sum_i \exp(i\underline{k}.\underline{R}_i) \mid k' \rangle \right|^2 = \mathbf{S}(k) \text{ structure factor of liquid}$$

=> 
$$\rho \sim [(e^2 v_F^2 N)^{-1} \int [V(k)]^2 S(k)]^4 (k/2k_F)^3 d(k/k_F)$$



#### Pre-irradiation conclusions

- 1. Free energy vs. kinetics -
  - FE considerations => · GFA in deep eutectics
    - rôle of ≠ phase structures & strain
    - · nucleation & growth of a vs. c phase
    - GFA when competing phases => "frustration"

Microscopic scale: related to atomic (+ vacancy) motion  $\rightarrow V_P, E_B, ... \Rightarrow ct. MD$ , KLMC...

- 2. Twofold rôle of chemical short range order (CSRO)
  - competing CSROs => favor GFA
  - CSRO in amorphous structures



- disorder => aperiodic potentials; mfp ~ nm
- · hence CSRO determines details of conductivity

#### Effect of irradiation/implantation

- 1. Free energy vs. kinetics -
  - FE considerations => · GFA in deep eutectics
    - · rôle of ≠ phase structures & strain
    - · nucleation & growth of a vs. c phase
    - GFA when competing phases => "frustration"

- Modifications forced atomic mobility
  - phase diagram (radiation-enhanced diffusion)
  - (i) open system; (ii) far from equilibrium (ergodicity?)
- 2. Twofold rôle of chemical short range order (CSRO)
  - · competing CSROs => favor GFA
  - · CSRO in amorphous structures

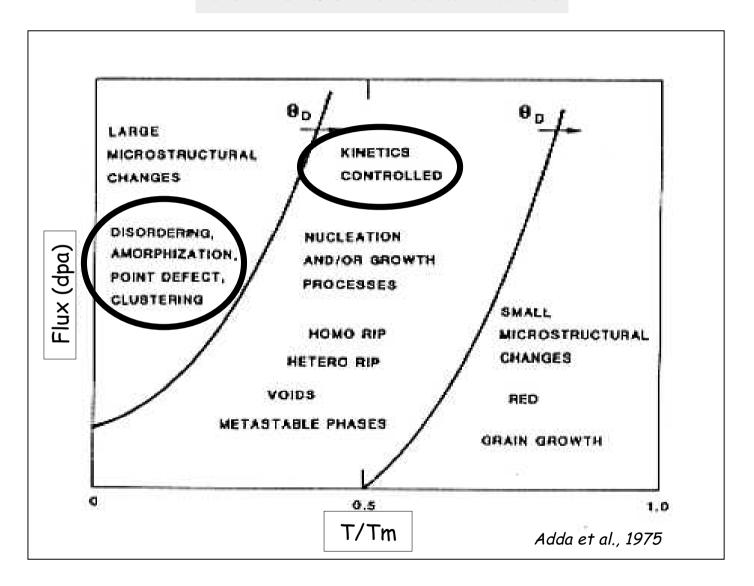
Does irradiation (atomic displacements) modify local stability criteria?

- 3. Transport and magnetic properties related to
  - disorder => aperiodic potentials; mfp ~ nm
  - hence CSRO determines details of conductivity

Sensitive to structure @ nanoscale (amorphization mechanism)

# Refer to thermodynamics (equilibrium vs. nonequilibrium)

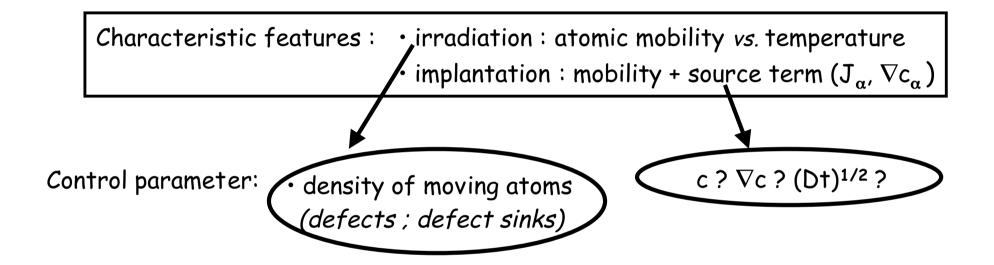
#### Solids under irradiation



#### Open systems: irradiation and implantation

"open system": • stability does not require potential minimization

· there may be no unique equilibrium state



Ergodicity: • a system is ergodic if ensemble average = time average  $(1/N) \sum_{1}^{N} [y^{(k)}(t)] = \langle y(t) \rangle = \langle y \rangle \Rightarrow stationary system (A, B) goes through all intermediate states$ 

irradiation ⇒ NON-ERGODIC

#### Analysis of open ("driven") systems

G. Martin & P. Bellon, Sol. State Phys. 50(1997)189 Mat. Sci. Forum 15-18(1987)1337 J.W.Cahn, Acta Met. 9(1961)795

Consider a 2-component system:

irradiation  $\rightarrow$  competition  $\begin{cases} \cdot \text{ random ballistic mixing } \rightarrow \text{ instability} \\ \cdot \text{ irrad.-enhanced diffusion } \rightarrow \text{ stability} \end{cases}$ 

Ballistic diffusion : 
$$\mathfrak{D}_{\mathbf{B}}^{\mathbf{*}}=c_{\mathbf{2}}\mathfrak{D}_{1}+c_{\mathbf{1}}\mathfrak{D}_{2}$$

Ballistic diffusion : 
$$\mathfrak{D}_{B}^{*}=c_{2}\mathfrak{D}_{1}+c_{1}\mathfrak{D}_{2}$$
 where  $\mathfrak{D}_{\alpha}=\frac{1}{2}$  or  $c_{\alpha}^{2}$  irrad. flux replacement cross-section

• ballistic interdiffusion flux 
$$J_1^B = J_2^B = -\mathfrak{D}_B^* N_v \partial c_2/\partial x$$
• irrad.-enhanced diffusion (~ JW Cahn)  $J_{diff} = -M^* N_v [f'' \partial c_2/\partial x - 2K \partial^3 c_2/\partial x^3]$ 

irrad.-enh. mobility 2d deriv.FE gradient E

where  $M^* = [c(1-c)/kT]D^* \rightarrow irrad.$ -enh. diffusion coeff.

Combine the 2 equations  $\rightarrow$  concentration profile that minimizes F.E.

(closed) 
$$F_{c}^{f}(x) = N_{v} \int \{f[c(x)] + K(dc/dx)^{2}\} dx$$
 ( $\rightarrow$  zero flux) (open)  $\psi \{c(x)\} = N_{v} \int \{\psi[c(x)] + K(dc/dx)^{2}\} dx$   $\rightarrow \psi \sim F.E.$ 

$$\psi \{c,T\} = f\{c,T'\}$$

Radiation Effects in Solids, Erice July 18-28, 2004

#### Open system under irradiation

G. Martin, Phys. Rev. 30 (1984) 1424

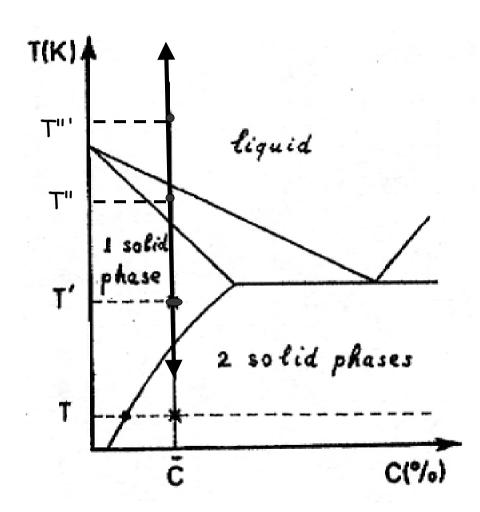
$$T' = (1+\Delta)T$$
$$\Delta = \mathfrak{D}_{B}^*/D^*$$

$$\Delta \propto \phi^{1/2} \exp(E_{\rm m}^{\rm v}/kT)$$

T': precipitate dissolution

T": coexistence between amorphous & crystalline phases

T"': amorphous phase



## On a microscopic (mechanistic) scale...

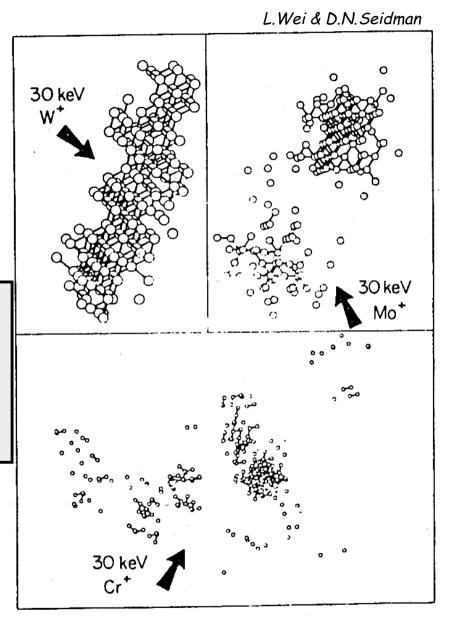
Irradiation-induced disordering & amorphization are

- kinetic
- non-ergodic

## Displacement cascade residues in W@RT

## Degree of disordering/amorphization depends on

- deposited energy density
- nature of bonding
- defect recombinations



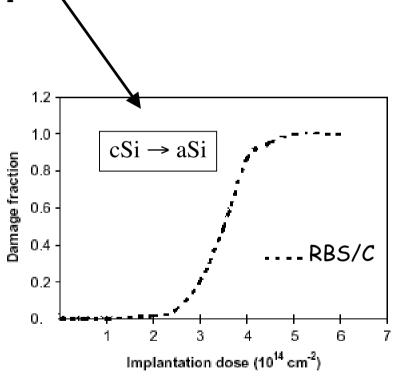
## Kinetic (collision-induced) amorphization

1. "Simple case 1" (ex: c-Si -> a-Si ?):
====Direct amorphization by each displacement cascade ====

$$\Rightarrow$$
  $\alpha(a/c) = [1-exp(-\sigma\Phit)] = P_1$ 

F. F. Morehead & B. L. Crowder, Rad. Eff. Def. Sol. 6(1970)27

(alternatively, any  $\Sigma$  of defect mechanisms will do !)



(L.C. Feldman, T. Picraux, 1978)

## Kinetic (collision-induced) amorphization

2. "Simple case 2 ": collision-induced amorphization

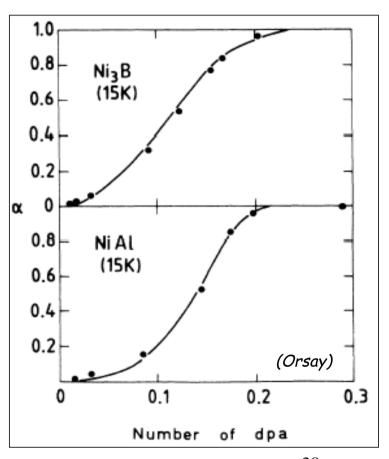
==== Need more than 1 impact to amorphize ====

Amorphization by displacement (cascade) overlap

=> 
$$\alpha = \sum_{n_c}^{\infty} [n^n \exp(-\sigma \Phi t)/n!] = P_n$$

J. F. Gibbons, Proc. IEEE 60(1972)1062

ex: c-Ni<sub>3</sub>B → a-Ni<sub>3</sub>B c-NiAl → a-NiAl (irrad. with keV D ions)



Kinetic (collision-induced) amorphization

3. <u>Johnson-Mehl-Avrami</u> mechanism:

nucleation+growth+overlap

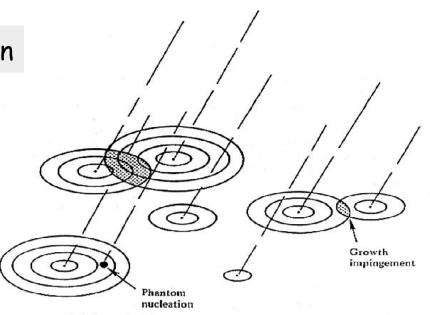
(→ involves duration of phase transformation)

=>  $\alpha = 1-\exp(-Kr^n)$  $K \sim R_N R_G^3 \exp(-\Delta H_N + 3\Delta H_G)/kT$ 

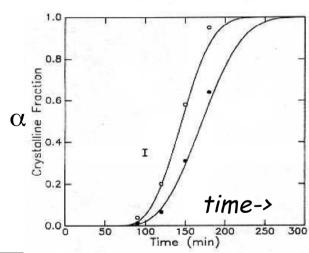
nucleation & growth rates

n = F(nucl. & growth modes) = 1, ...4...

Note! ~ same sigmoidal shape as #2

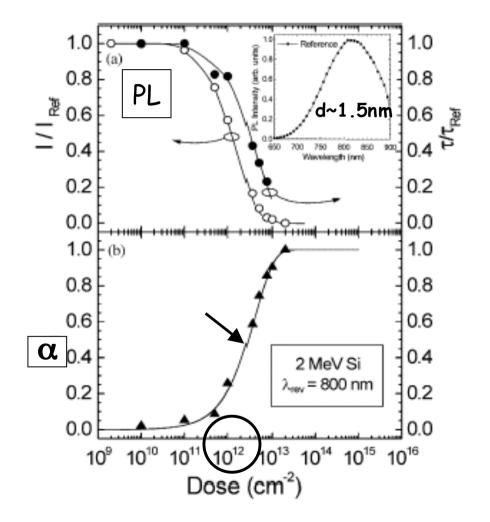


A schematic picture depicting the falling of raindrops on the surface of a pond. The overlapping of ripples (growth impingement) and a later raindrop fallings within a ripple (phantom nucleation) are indicated.



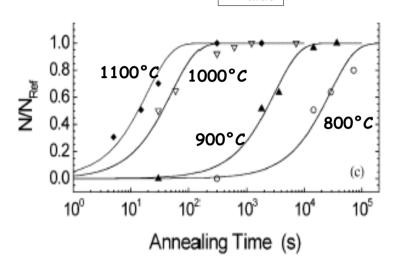
Importance: Interface growth, where ballistic mixing competes with growth via diffusion/migration

# Rôle of interfaces: Amorphization & recrystallization of Si nanoclusters in SiO<sub>2</sub>



D. Pacifici, G. Franzò et al, Physica E 16(2003)404

Irradiate by Si(2 MeV)

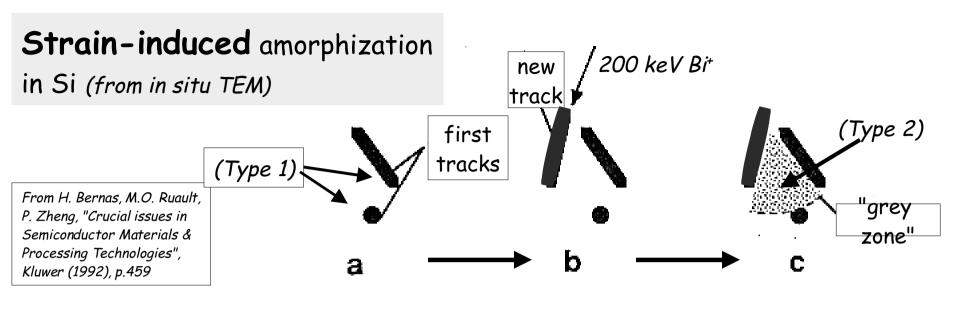


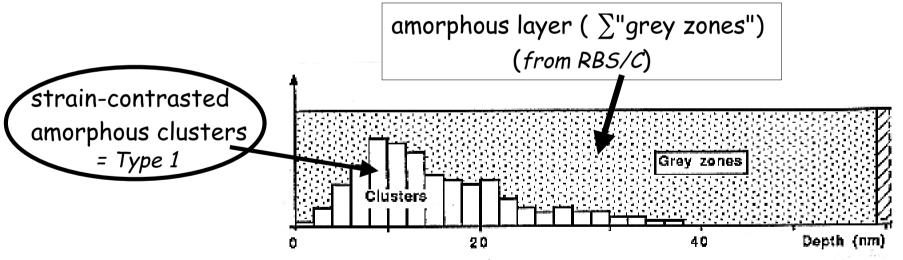
$$\frac{N}{N_{\text{Ref}}} = 1 - \exp\left(-\frac{t}{\tau_{\text{c}}}\right) \qquad ??$$

 $\tau_c$  = recrystallization time

Nanoclusters vs. bulk:

- amorphization faster
- recrystallization slower Rôle of interface





Note:  $T_{evol} \sim 1$  second @ RT;  $T_{ann}$ (Type 1) ~500K;  $T_{ann}$ (Type 2) ~800K

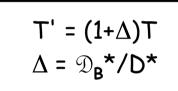
Implantation = Irradiation + compositional change:

Progressive c/a phase transformation

Building the amorphous structure from CSRO

## Progressive amorphization of Ni-P via implantation

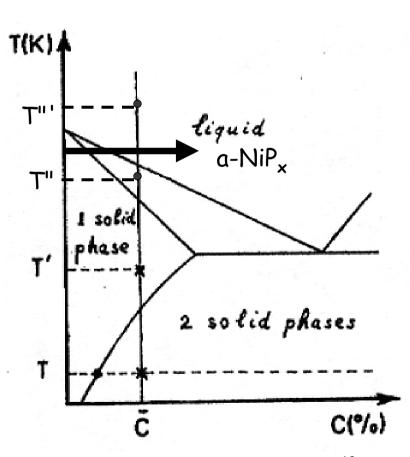
- ~ constant atomic displacement rate  $\rightarrow \mathfrak{D}_{B}^{*}/D^{*}=cst.$  (total=100 dpa!)
- · constant rate of P concentration increase



T': precipitate dissolution

T": coexistence between amorphous & crystalline phases

T"': amorphous phase



## Progressive amorphization of Ni-P via implantation (2)

### Questions

- @ low T "basic" amorphization mechanism:

kinetics>TD: rôle of GFA?

- @ higher T, competition: kinetics vs. growth
- new properties of the implantation-induced amorphous state ?

### The experiments

- Progressive implantation of P in Ni single crystals
- in situ TEM @ 15K & 300K: Diffraction studies
- RBS/C @ 80K & 300K: dechanneling studies

#### Results

- 1 phase (Ni+εP) → 2 phases (c-Ni + a-Ni<sub>0.88</sub>P<sub>0.12</sub>) → 1 phase (a-Ni<sub>0.85</sub>P<sub>0.15</sub>)
- "building block" of a-NiPx: the stable amorphous cluster
- confirmation via magnetic properties

Complementary information from in situ TEM: Strain

## Amorphization of Ni-P<sub>x</sub> @ 80K

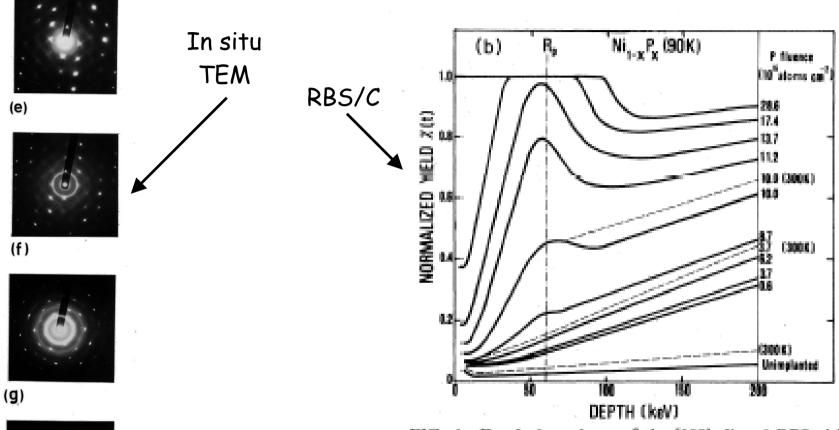


FIG. 4. Depth dependence of the [100]-aligned RBS yields normalized to the random yields for P-implanted Ni single crystal at LNT. Phosphorus-ion-implantation energy, 125 keV; analyzing particles, 380-keV <sup>4</sup>He ions.

M. Schack, MO Ruault et al; C. Cohen et al., PRB (1986)

Ni/P<sup>+</sup>50keV Phase Transformations-3 H. Bernas

(h)

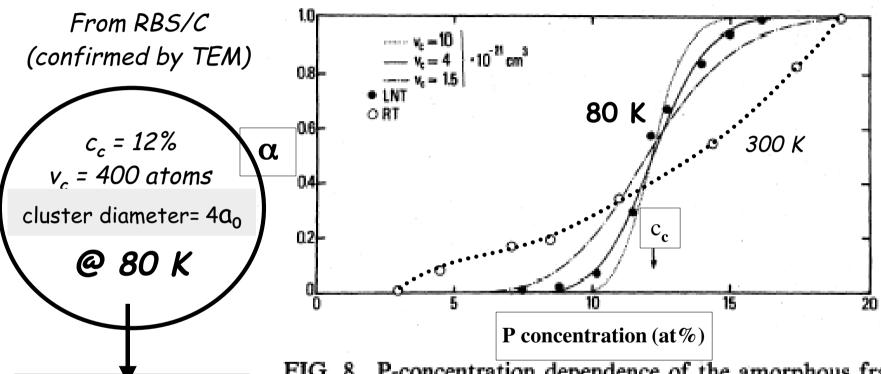
## Amorphization of Ni- $P_x$ @ 80K: the amorphization mechanism

From **TEM** & RBS/C, assume heterogeneous compound:

- amorphous clusters + crystalline host
- atomic displacements play ~ no rôle @ >1 dpa
  - · amorphous clusters are
    - stabilized by a minimum amount of P atoms  $N_c$
    - all identical
    - irradiation → relaxation
    - => · macroscopically, nonequilibrium system
      - microscopically, minimize configurational energy via clustering
- in implanted profile, divide volume  $\rightarrow v_c$ ; ave.nbr. P atoms =  $\underline{n}$ , probability distribn. is  $P(n)=(\underline{n})^n \exp(-\underline{n})/n!$
- => amorphous fraction is

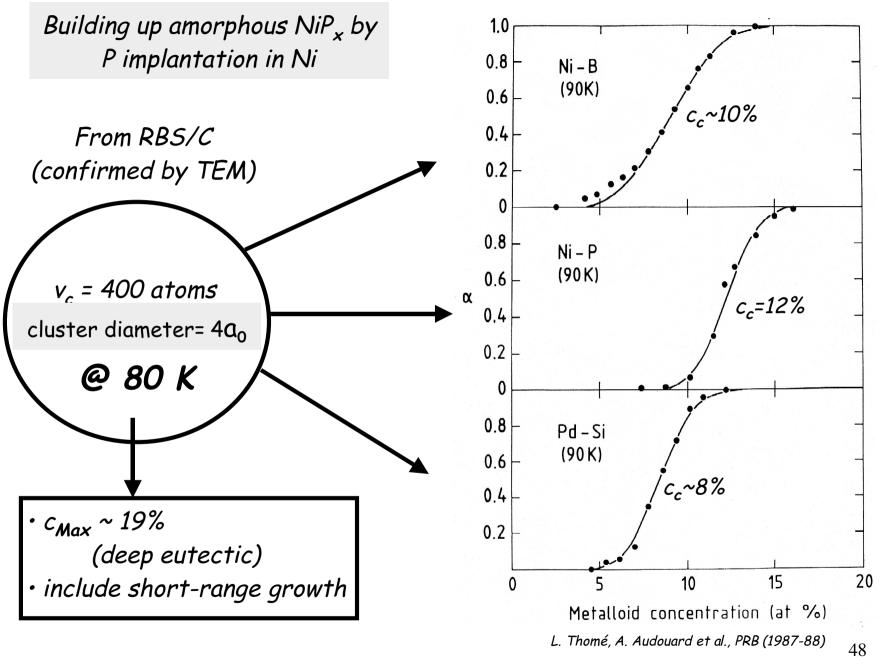
$$\alpha = \sum_{Nc}^{\infty} [(\underline{n})^n \exp(-\underline{n})/n!]$$

## Building up amorphous $NiP_x$ by P implantation in Ni

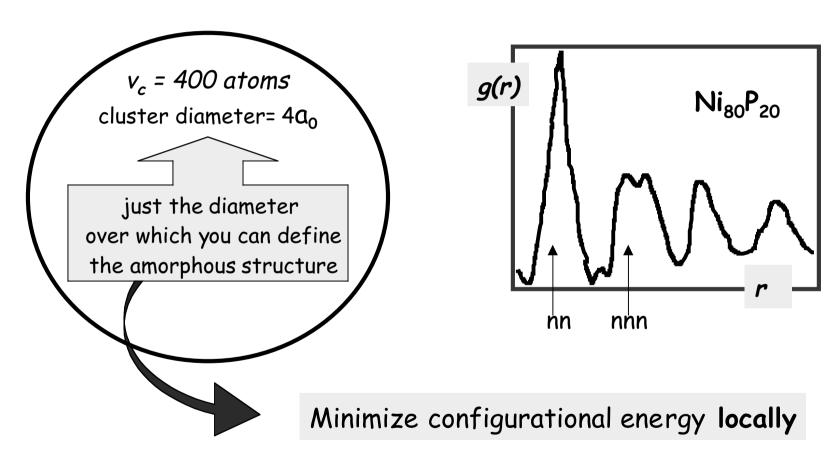


· c<sub>c</sub> = 19% (deep eutectic) · include SRO growth **@ 300K** 

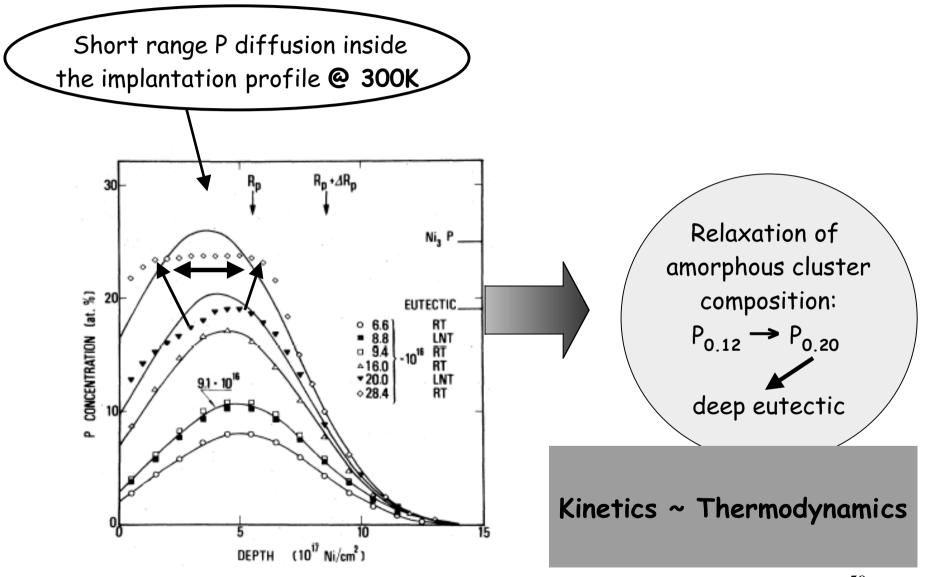
FIG. 8. P-concentration dependence of the amorphous fraction  $\alpha$  for LNT (solid circles) and RT (open circles) implants. The solid line represents the best fit to the LNT experimental data using Eq. (4). Dashed lines are calculated, using Eq. (4), with different elementary volumes  $v_c$  of the amorphous clusters



## Stability criterion for building the amorphous phase



H. Bernas et al., (1986)



## Consequences of strain as amorphization proceeds

- defect bands :

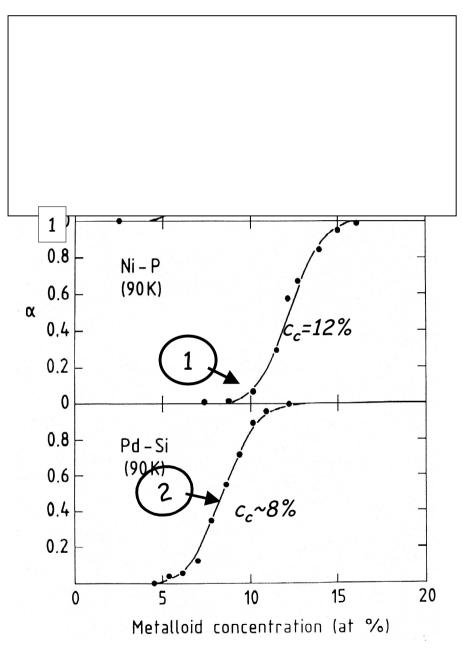
tearing (1)

irrad-induced creep & flow:the chewing-gum effect (2)

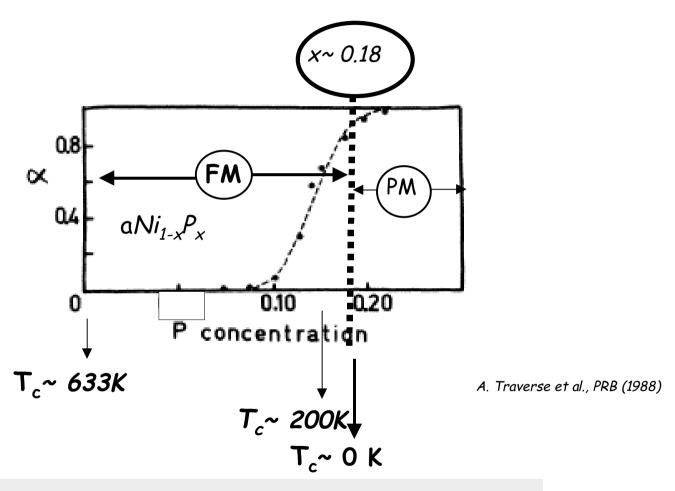
MO Ruault, M. Schack et al., 1988

See film





## Conduction/magnetic properties: Hall resistivity & EHE in $Ni_{1-x}P_x$ :



Expected from work on "macroscopic" Metglass: Magnetism disappears @  $c \rightarrow a$  transformation ?

ture." The resistivity was measured at 4.2 K after each implantation step and, using ac measurements, the Hall voltage was followed against the magnetic induction at 4.2 K and in some cases at 80 K.

#### IV. HALL EFFECT IN Ni AND ITS ALLOYS

The Hall resistivity  $\rho_H$  is given by

$$\rho_H = V_H t / I$$
, (1)

where  $V_H$  is the Hall voltage, t the sample thickness, and I the current. An experimental  $V_H$  versus B curve, obtained in a magnetic sample such as Ni (shown in Fig. 3 for x = 0.0) can be described empirically by the following formula in SI units, using the notation of Hurd:<sup>11</sup>

$$\rho_H = (R_0B + R_SM)\mu_0, \qquad (2)$$

where M is the magnetization in A/m,  $\mu_0$  the vacuum magnetic permeability, and B the applied induction in T. The ordinary Hall coefficient  $R_0$ , expressed in  $m^3/A$  s, accounts for the Lorentz force acting on the electrons, while  $R_S$ , the spontaneous Hall coefficient expressed in the same units, is a characteristic contribution for magnetic materials. If B is written in terms of the internal magnetic field  $H_i$ , Eq. (2) becomes

$$B = (H_i + NM)\mu_0$$
,  
 $\rho_H = (R_0H_i + R_1M)\mu_0$  with  $R_1 = R_0 + R_S$ ,
  
(3)

where  $R_1$  is the extraordinary Hall coefficient and N the demagnetization factor, equal to unity in thin films. For low B values, the slope at the origin of  $\rho_H$  versus B is  $R_1$ . When all the domains are aligned, the spin saturation is reached, the magnetization is  $M_2$ , and the Hall voltage is linear versus B with a slope  $R_0$ .

In the low-field regime, the normal Hall coefficient  $R_0$  is equal to  $1/n^*e$ , in a free-electron model, where  $n^*$  is the effective number of charges per unit volume. In Ni,  $R_0$  is negative, is indicating electronic conduction.

As shown by Hurd, 11 the spontaneous Hall coefficient  $R_S$  (negative in Ni) is

$$R_S \propto \rho_0^2 \sigma_H^{(1)}$$
, (4)

where  $\sigma_H^{(1)}$  only depends on the spin of the system and  $\rho_0$ is its residual resistivity.

Previous Hall-effect measurements on the thin Ni films, performed by Le Bas, had revealed the existence of an easy magnetization axis inducing a remanent magnetization vector in the absence of applied induction, tilted at an angle to the film plane. This affects both the initial slope of the Hall resistivity (the measured quantities  $R_1$  and  $R_S$  become  $R_1'$  and  $R_S'$ ), and the saturation magnetization (which is now  $B_S$  instead of  $M_S$ ,  $B_S$  being the projection of  $M_S$  on the applied field direction). These film effects also depend on evaporation conditions and subsequent annealing treatments.

The magnitude of  $R_0$  is affected by alloying at concentrations high enough to modify the band structure and consequently the number of charges per unit volume. 

Through  $\rho_0$ ,  $R_S$  is strongly correlated to the disorder in the sample, as experimentally shown in several cases. 

14

In the paramagnetic state, which is reached for  $x \sim 0.18$  in  $Ni_{1-x}P_x$ , the Hall resistivity must be linear with H:

$$\rho_H = (R_0 + R_s \chi)H, \qquad (5)$$

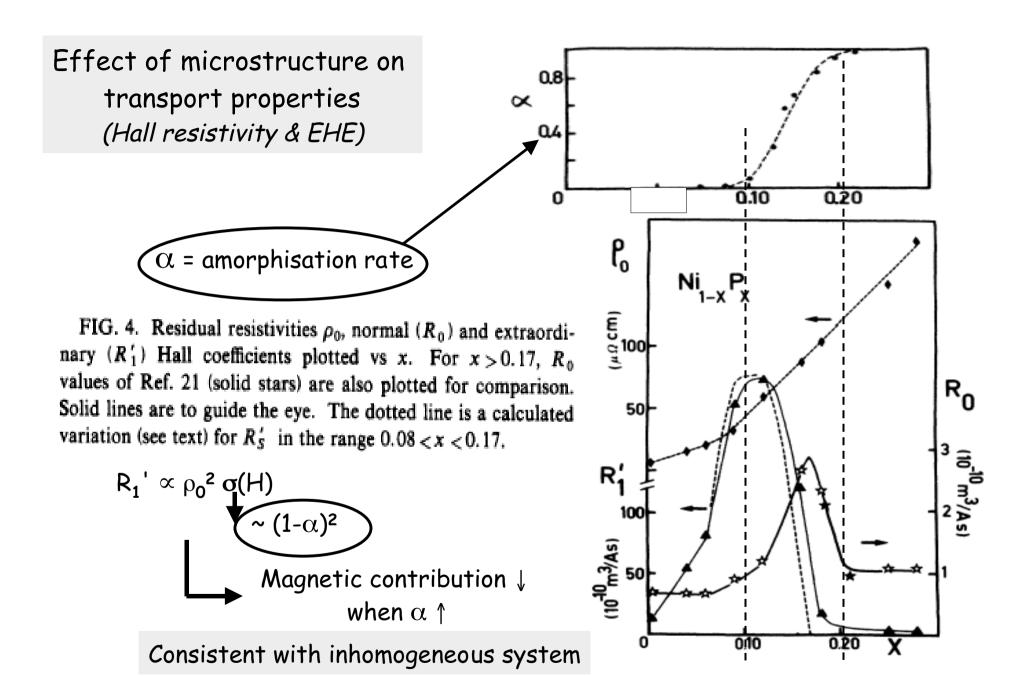
where X is the magnetic susceptibility. 11

#### V. RESULTS

The values of  $R_0$ ,  $R_1'$ , and  $R_S'$ , equal to  $R_1' - R_0$ , were found to be negative, in Ni films whatever the P concentration from 0 up to 0.28; hence, in the following we have omitted the negative sign and only presented the absolute values.

#### A. On pure Ni films

In agreement with the results of Le Bas, our measured average value of  $B_S$  is 0.48 T (the bulk value being 0.6 T). Our values of  $R_1'$  [typically (10.39±1.50)  $\times 10^{-10}$  m<sup>3</sup>/As for 550 < t < 1950 Å] agree with those



## Amorphization via implantation: the mechanism

Kinetics vs. Thermodynamics

Ergodicity? (no random disordering)

## Control parameter @ LT =

- atomic displacement rate (+ solute atom flux)
- · chemical short range order (CSRO)

Varies as f(T)(relate to F.E. curves)
determines stability criterion

Note compatibility with Martin's approach

#### General references

- L. Landau and E.M. Lifschitz, "Statistical Physics", Addison-Wesley (1958)
- F. Reif "Fundamentals of Statistical & Thermal Physics", McGraw Hill (1965)
- J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 28 (1958) 258; 30 (1959) 1121; 31 (1959) 688
- K. Binder, Repts. Progr. Phys. **50**(1987)783
- R. M. White and T. W. Geballe, "Order and Disorder in Solids", J. Wiley, NY (1987)

#### Others

- K. R. Kelton, A. L. Greer and C. V. Thompson, J. Chem. Phys. 79(1983)6261
- J. H. Perepezko, Prog. Mater. Sci. 49 (2004) 263 and refs therein
- G. Martin and P. Bellon, Sol. State Phys. 50 (1997) 189, and refs. therein
- F. Spaepen, Sol. State Phys. **50** (1997)
- "Glassy Metals", ed. R. Hasegawa, CRC Reviews (1990)
- C. Cohen et al., Phys. Rev. B31(1985)5

(and see refs. in Paolo Ossi's lecture)